# Chapter 3
# Mercury in Atmospheric Components

## 3.1 Results

From June 11, 1994 to October 30, 1995, atmospheric samples were collected from five shoreline sampling station and one out-of-basin sampling station (Table 3-1 and Figure 2-2 in Chapter 2). Atmospheric samples were collected from three separate sampling media or phases: vapor ($ng/m^3$), particulate ($pg/m^3$) and precipitation (ng/L). A total of 387 vapor phase samples, 399 particulate phase samples, and 407 precipitation phase samples were collected and analyzed for total mercury.

Table 3-1. Numbers of Atmospheric Samples Analyzed for Mercury

| Sampling Station | | Sampling Dates | Number of Vapor Samples Analyzed | Number of Particulate Samples Analyzed | Number of Precipitation Samples Analyzed | Total Samples Analyzed |
|---|---|---|---|---|---|---|
| Shoreline Atmospheric Sampling Stations | Chiwaukee Prairie | 7/19/94 to 10/30/95 | 73 | 79 | 74 | 226 |
| | George Washington H.S. | 7/19/94 to 7/25/94 | 1 | 2 | 0 | 3 |
| | IIT Chicago | 6/11/94 to 10/30/95 | 80 | 83 | 74 | 237 |
| | Sleeping Bear Dunes | 6/23/94 to 10/30/95 | 80[1] | 80 | 97 | 257 |
| | South Haven | 6/19/94 to 10/30/95 | 79 | 81 | 81 | 241 |
| Out-of-basin Atmospheric Sampling Stations | Bondville | 6/24/94 to 10/30/95 | 74 | 74 | 81 | 229 |
| Total | | | 387 | 399 | 407 | 1193 |

[1] One sample was invalid.

### 3.1.1 Vapor Fraction

Between 73 and 80 vapor-phase samples were collected from four shoreline atmospheric stations and one out-of-basin station (Bondville, located in Illinois). In addition, one sample was collected at George Washington High School. Because of the representativeness issues with using a single sample, this result was not used in any of the analyses. The overall mean vapor-phase concentration was 2.44 $ng/m^3$.

Table 3-2. Mean Mercury Concentrations Measured in the Vapor Phase

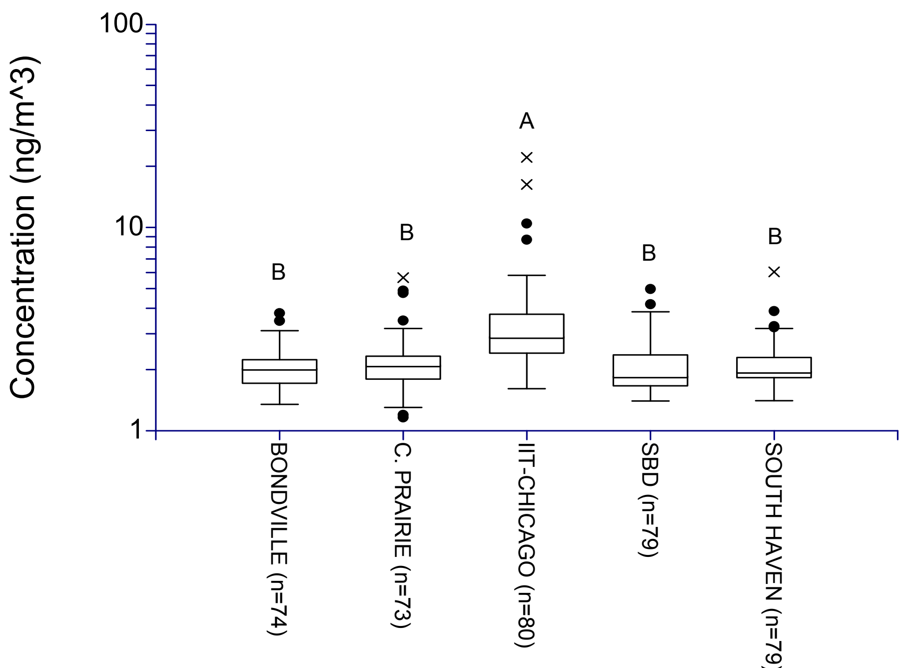
| Sampling Station | N | Mean ($ng/m^3$) | Median ($ng/m^3$) | Range ($ng/m^3$) | SD ($ng/m^3$) | RSD (%) | Below DL (%) |
|---|---|---|---|---|---|---|---|
| Chiwaukee Prairie | 73 | 2.20 | 2.10 | 1.16 to 5.68 | 0.740 | 33.6 | 0 |
| George Washington H.S. | 1 | 2.31 | 2.31 | NA | NA | NA | 0 |
| IIT Chicago | 80 | 3.62 | 2.90 | 1.61 to 22.2 | 2.89 | 80.0 | 0 |
| Sleeping Bear Dunes | 79 | 2.12 | 1.86 | 1.40 to 4.99 | 0.694 | 32.8 | 0 |
| South Haven | 79 | 2.16 | 1.96 | 1.41 to 6.05 | 0.647 | 29.9 | 0 |
| Bondville | 74 | 2.06 | 2.03 | 1.35 to 3.80 | 0.469 | 22.7 | 0 |

NA = Not applicable

### *3.1.1.1 Geographical Variation*

Mean vapor-phase mercury concentrations ranged from 2.06 ng/m$^3$ at Bondville to 3.62 ng/m$^3$ at IIT Chicago (Table 3-2). The mean concentration at IIT Chicago was significantly greater than those of the other stations, based on an analysis of variance (ANOVA) model with the Tukey method for pairwise comparisons (results log-transformed prior to analysis). This was to be expected, because this station was the only one classified as an urban sampling location. Among the remaining stations, only Chiwaukee Prairie was located within 10 km of an urban area. The maximum concentration of 22.2 ng/m$^3$ observed at IIT Chicago was more than three times greater than the highest concentration observed at any of the other stations (6.05 ng/m$^3$ at South Haven). The differences in mercury concentrations at the five stations are shown in Figure 3-1.

Figure 3-1. Mercury Concentrations in Atmospheric Vapor Measured at Four Lake Michigan Shoreline Sites and One Out-of Basin Site (Bondville)

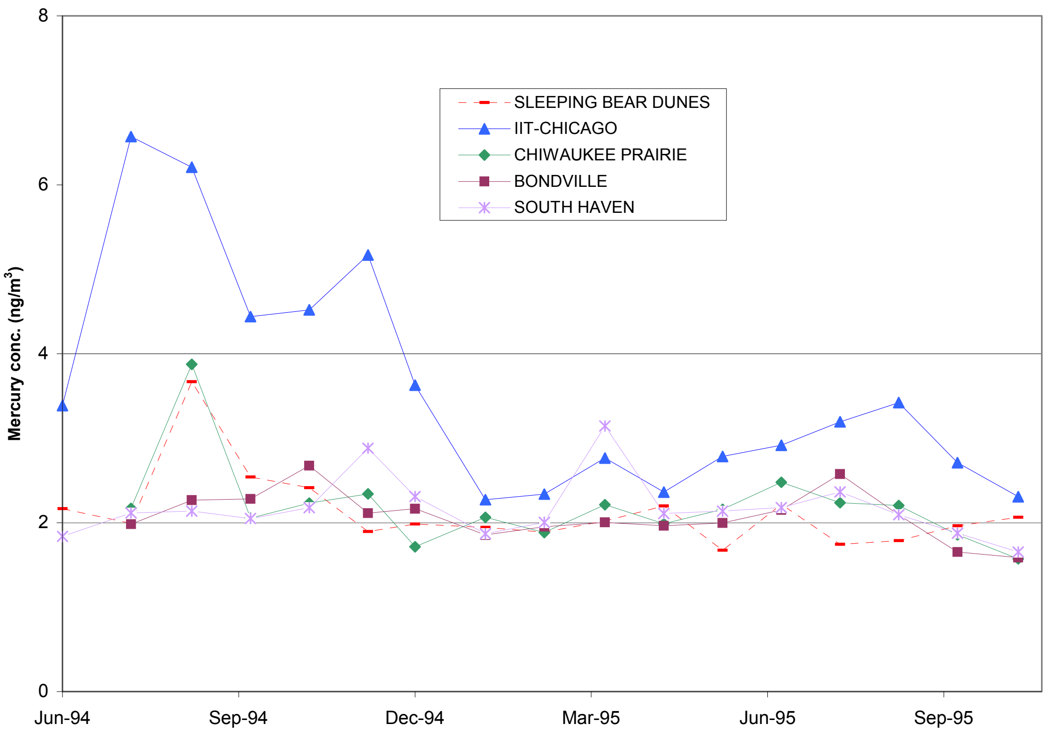



Boxes represent the 25th (box bottom), 50th (center line), and 75th (box top) percentile results. Bars represent the results nearest 1.5 times the inter-quartile range (IQR=75th-25th percentile) away from the nearest edge of the box. Circles represent results beyond 1.5*IQR from the box. Xs represent results beyond 3*IQR from the box. Letters above the boxes represent results of analysis of variance and multiple comparisons test. Boxes with the same letter were not statistically different (at alpha = 0.05). The George Washington High School sampling site was not included in the analysis of variance due to the small number of samples. C. Prairie = Chiwaukee Prairie, SBD=Sleeping Bear Dunes

### *3.1.1.2 Seasonal Variation*

Beginning in July 1994, samples were collected approximately weekly at each station. Therefore, there were multiple results from each station for each month in this interval, as well as one to two results during June 1994 at three of the stations. A time plot of the monthly mean concentrations from each station is presented in Figure 3-2.

Figure 3-2. Arithmetic Monthly Means at each Station - Vapor Phase




At IIT Chicago, there appears to be a difference in concentrations between the years 1994 and 1995. With the exception of June 1994, for which only 2 samples were collected, the monthly means from 1994 are greater than any of the monthly means for 1995. Based on a two-sample *t*-test using Satterthwaite's correction for differences in variability, this annual difference is significant ($p<0.0001$; using individual log-transformed results). Annual differences are less noticeable for the other stations, however, the means were significantly greater in 1994 for Bondville ($p=0.0328$) and Sleeping Bear Dunes ($p=0.0058$). These differences may have been due to seasonality rather than annual shifts, as most samples collected in the winter were collected in 1995.

Peaks occurred at IIT Chicago during July and August 1994, November 1994, and August 1995. Many of the other stations also had peaks during summer months. For example, the maximum monthly means for Sleeping Bear Dunes and Chiwaukee Prairie occurred during August 1994. At Bondville, the maximum mean occurred during October 1994. At South Haven the maximum concentration occurred in March 1995, and in fact exceeded the mean at IIT Chicago during that month. After classifying individual sample results according to season based on the collection date, significant differences between seasons occurred at IIT Chicago ($p=0.0014$) and Chiwaukee Prairie ($p=0.0228$), but not the other stations, based on a one-way ANOVA model, with results log-transformed prior to analysis. At IIT Chicago, the mean concentration during summer was significantly greater than the means of sample concentrations collected during spring and winter, based on the Tukey method for pairwise comparisons. At Chiwaukee Prairie, the mean concentration of samples collected during summer was significantly greater than the mean concentration during autumn.

### 3.1.2 Particulate Fraction

Between 74 and 83 particulate-phase samples were collected from four shoreline atmospheric stations and one out-of-basin station (Bondville). In addition, two samples were collected at George Washington High School. Because of the representativeness issues with using only two samples, these results were not used in any of the analyses. The overall mean particulate-phase concentration was 30.7 pg/m$^3$.

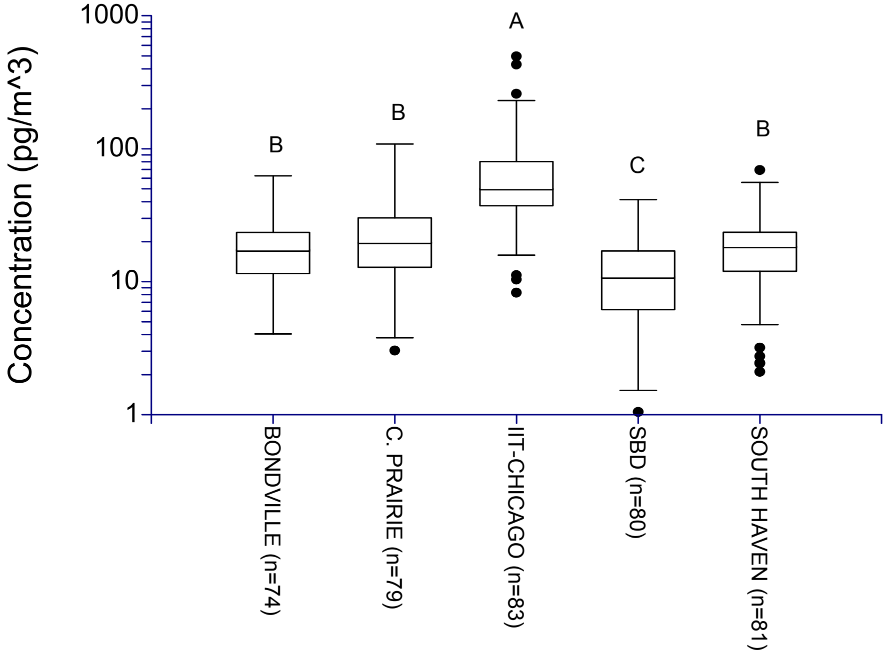
Table 3-3. Mean Mercury Concentrations Measured in the Particulate Phase

| Sampling Station | N | Mean (pg/m$^3$) | Median (pg/m$^3$) | Range (pg/m$^3$) | SD (pg/m$^3$) | RSD (%) | Below DL (%) |
|---|---|---|---|---|---|---|---|
| Chiwaukee Prairie | 79 | 24.0 | 19.9 | 3.03 to 108 | 18.2 | 75.6 | 0 |
| George Washington H.S. | 2 | 151 | 151 | 58.6 to 244 | 131 | 86.7 | 0 |
| IIT Chicago | 83 | 73.7 | 50.4 | 8.25 to 494 | 77.2 | 105 | 0 |
| Sleeping Bear Dunes | 80 | 12.1 | 10.9 | 1.05 to 41.3 | 8.28 | 68.2 | 0 |
| South Haven | 81 | 19.3 | 18.5 | 2.10 to 69.0 | 12.2 | 63.1 | 0 |
| Bondville | 74 | 18.7 | 17.4 | 4.04 to 62.5 | 11.0 | 58.8 | 0 |

#### *3.1.2.1 Geographical Variation*

Mean particulate-phase mercury concentrations ranged from 12.1 pg/m$^3$ at Sleeping Bear Dunes to 73.7 pg/m$^3$ at IIT Chicago (Table 3-3). The mean concentration at IIT Chicago was greater than the maximum concentrations at all stations other than Chiwaukee Prairie. Based on an ANOVA model with the Tukey method for pairwise comparisons, the mean concentration at IIT Chicago was significantly greater than those of the other stations and the mean concentration at Sleeping Bear Dunes was significantly lower than those of the other stations (results log-transformed prior to analysis). These differences are not unexpected, given the locations of the different stations. In addition to IIT Chicago being the only station located in an urban area, Sleeping Bear Dunes is the only station located more than 50 km from an urban area. The differences in mercury concentrations at the five stations are shown in Figure 3-3.

Figure 3-3. Mercury Concentrations in Atmospheric Particles Measured at Five Lake Michigan Shoreline Sites and One Out-of Basin Site (Bondville)




Boxes represent the 25th (box bottom), 50th (center line), and 75th (box top) percentile results. Bars represent the results nearest 1.5 times the inter-quartile range (IQR=75th-25th percentile) away from the nearest edge of the box. Circles represent results beyond 1.5*IQR from the box. Letters above the boxes represent results of analysis of variance and multiple comparisons test. Boxes with the same letter were not statistically different (at alpha = 0.05). The George Washington High School sampling site was not included in the analysis of variance due to the small number of samples.
C. Prairie = Chiwaukee Prairie, SBD = Sleeping Bear Dunes

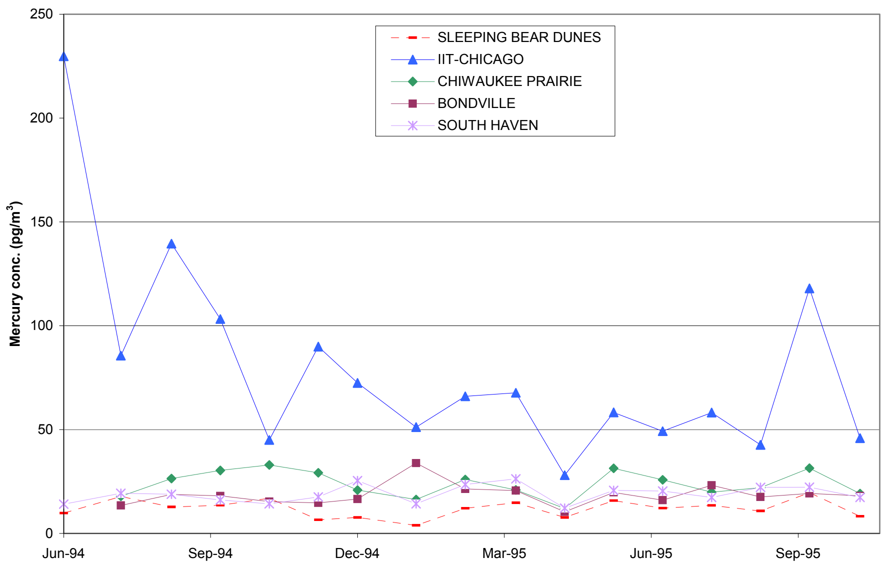
### *3.1.2.2 Seasonal Variation*

Beginning in July 1994, samples were collected approximately weekly at each station. Therefore, there were multiple results from each station for each month in this interval, as well as one to two results during June 1994 at three of the stations. A time plot of the monthly mean concentrations from each station is presented in Figure 3-4.

Particulate sample concentrations from IIT Chicago seem to exhibit the same annual difference observed in vapor samples, although to a lesser extent. Three of the four highest concentrations at IIT Chicago occurred during 1994. However, it is worth noting that the June 1994 maximum was based on only two samples and is therefore more variable than the other monthly means, which were based on at least four samples. The difference between years was significant for IIT Chicago ($p=0.0456$), but not for the other stations, based on a two-sample *t*-test run on the individual log-transformed results, with Satterthwaite's correction for differences in variance.

Other than IIT Chicago, the stations did not exhibit much variability between months and there was little evidence of any effects of seasonality. There was some consistency between these stations during May 1995, when all stations had relative minimum concentrations, and in September 1995, when all stations had relative maximum concentrations. Mercury concentrations differed significantly between seasons only at Sleeping Bear Dunes (p=0.0311), based on a one-way ANOVA model with the Tukey method for pairwise comparisons (results log-transformed prior to analysis). For this station, the mean concentration of samples collected in summer was significantly greater than the mean concentration in winter.

Figure 3-4. Arithmetic Monthly Means at each Station - Particulate Phase




### 3.1.3 Precipitation Fraction

Between 74 and 97 precipitation-phase samples were collected from four shoreline atmospheric stations and one out-of-basin station (Bondville, located in Illinois). The overall mean precipitation-phase concentration was 20.6 ng/L.

Table 3-4. Mean Mercury Concentrations by Station Measured in the Precipitation Phase

| Sampling Station | N | Mean (ng/L) | Volume-weighted Mean (ng/L) | Median (ng/L) | Range (ng/L) | SD (ng/L) | RSD (%) | Below DL (%) |
|---|---|---|---|---|---|---|---|---|
| Chiwaukee Prairie | 74 | 23.1 | 16.5 | 19.9 | 4.47 to 134 | 18.3 | 79.1 | 0 |
| IIT Chicago | 74 | 26.1 | 21.1 | 20.4 | 5.45 to 74.6 | 15.5 | 59.5 | 0 |
| Sleeping Bear Dunes | 97 | 15.2 | 11.0 | 11.0 | 2.09 to 63.7 | 12.0 | 78.9 | 0 |
| South Haven | 81 | 18.1 | 13.9 | 14.9 | 3.21 to 110 | 14.8 | 81.9 | 0 |
| Bondville | 81 | 22.1 | 16.1 | 16.3 | 5.32 to 137 | 18.3 | 82.5 | 0 |

#### *3.1.3.1 Geographical Variation*

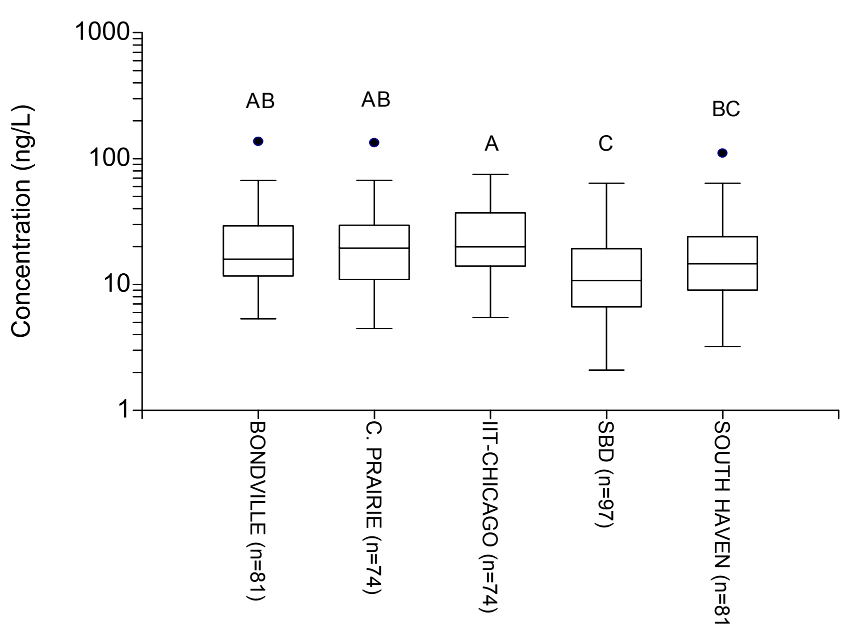
Mean precipitation-phase mercury concentrations ranged from 15.2 ng/L at Sleeping Bear Dunes to 26.1 ng/L at IIT Chicago (Table 3-4). In addition to the mean concentrations listed, means were also calculated on a volume-weighted basis, which ranged from 11.0 ng/L at Sleeping Bear Dunes to 21.1 ng/L at IIT Chicago. Volume-weighting was done to minimize biases occurring due to small precipitation events (low bias). The variability of the sample volumes collected at each station was high, with relative standard deviations (RSDs) of approximately 100%. However, the volumes themselves did not differ greatly between stations, and the differences in volume-weighted means between stations were consistent with the differences in arithmetic means. The formula for volume-weighted means is presented below:

$$\frac{\sum_{i=1}^{n} c_i \times v_i}{\sum_{i=1}^{n} v_i}$$

where: $c_i$ = measured concentration in the *i*th sample,
$v_i$ = volume of the *i*th sample, and
n = number of samples.

Arithmetic means were compared using a one-way ANOVA model with the Tukey method for pairwise comparisons. The mean concentration at Sleeping Bear Dunes was significantly lower than those at IIT Chicago, Bondville, and Chiwaukee Prairie, and the mean concentration at South Haven was also significantly lower than that at IIT Chicago. The difference between IIT Chicago and the other stations for the precipitation phase is smaller than for the vapor and particulate phases. This is likely due to the lack of an extremely high concentrations collected from this station. During a rain event, mercury is very rapidly flushed out the atmosphere; hence, the first rain during an event has the highest mercury concentrations. Therefore, short duration rain events have higher mercury concentrations than long duration events because the lower mercury concentrations of rain later in an event tend to dilute the high concentrations received early in an event. The differences in mercury concentrations at the five stations are shown in Figure 3-5.

Figure 3-5. Mercury Concentrations in Atmospheric Precipitation Measured at Four Lake Michigan Shoreline Sites and One Out-of-basin Site (Bondville)



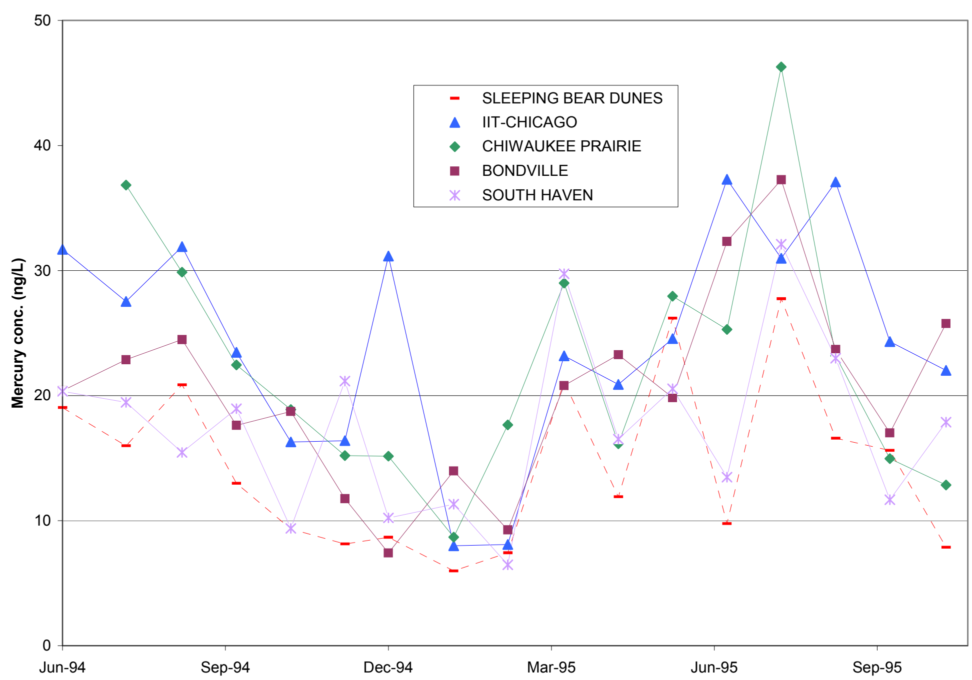

Boxes represent the 25th (box bottom), 50th (center line), and 75th (box top) percentile results. Bars represent the results nearest 1.5 times the inter-quartile range (IQR=75th-25th percentile) away from the nearest edge of the box. Circles represent results beyond 1.5*IQR from the box. Letters above the boxes represent results of analysis of variance and multiple comparisons test. Boxes with the same letter were not statistically different (at alpha = 0.05). C. Prairie = Chiwaukee Prairie, SBD = Sleeping Bear Dunes.

### 3.1.3.2 Seasonal Variation

Beginning in June 1994, samples were collected at least once during each month at each station except for Chiwaukee Prairie, based on the occurrence of precipitation events. Sampling at Chiwaukee Prairie began in July 1994. Monthly mean concentrations were calculated directly and through volume-weighting at each station, and are presented as time plots in Figures 3-6 and 3-7, respectively.

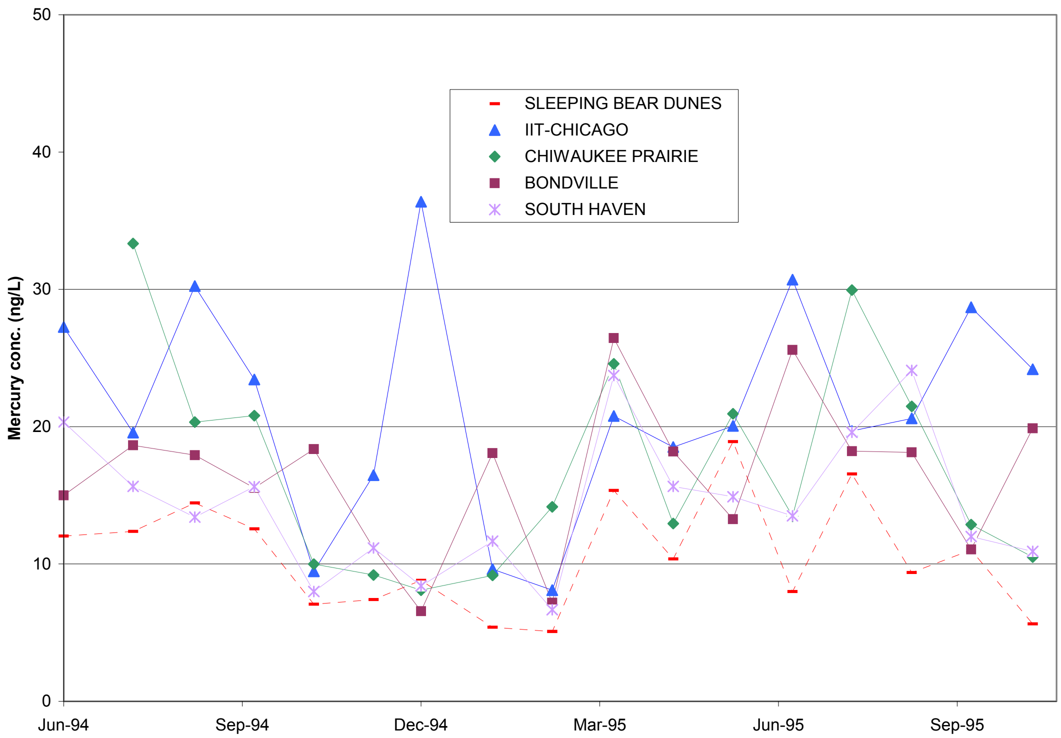
Generally, a seasonal pattern can be seen when looking at the arithmetic means, with concentrations greatest during the summer, and lowest during the winter. The only exception to this occurred in December 1994 at IIT Chicago, which had a relatively high mean concentration of 31.2 ng/L. The maximum monthly mean occurred in July 1995 for all stations except IIT Chicago, for which it occurred in June 1995. Based on one-way ANOVA models using the Tukey method for pairwise comparisons, there were significant differences in mean concentration between seasons at four of the five stations (Bondville: p=0.0166, Chiwaukee Prairie: p=0.0045, IIT Chicago: p=0.0170, Sleeping Bear Dunes: p=0.0008). At Chiwaukee Prairie, the mean concentration in summer was significantly greater than the mean concentration in autumn, while the mean concentration in summer was greater than the mean in winter at IIT Chicago. At Sleeping Bear Dunes, the mean concentration in summer was significantly greater than those in both autumn and winter, and the mean concentration in spring was also greater than the mean in autumn. No significant pairwise differences were found at Bondville. Unlike the vapor and particulate phases, there were no significant differences between years for any of the stations.

Figure 3-6. Arithmetic Monthly Means at each Station - Precipitation Phase




The seasonal pattern is less distinct when examining the volume-weighted means. Maximum monthly volume-weighted means occurred in different seasons for each station: in July 1994 at Chiwaukee Prairie, in March 1995 at Bondville, in May 1995 at Sleeping Bear Dunes, in August 1995 at South Haven, and in December 1994 at IIT Chicago. This last mean was the maximum at all stations, and contradicts the expectations based on the seasonal patterns exhibited in Figure 3-6. This value was based on three samples, including one collected on December 4, 1994, with a volume of 170 mL and a concentration of 60.2 ng/L. All other precipitation samples with concentrations exceeding 60 ng/L had sample volumes ranging from 22 to 83 mL. Therefore, this sample had a greater effect on the monthly volume-weighted mean concentration than other high concentration, lower-volume samples. For example, a sample collected at South Haven one week before had a concentration of 63.6 ng/L, but a volume of only 34 mL.

Figure 3-7. Volume-Weighted Monthly Means at each Station - Precipitation Phase




## 3.2 Quality Implementation and Assessment

As described in Section 1.5.5, the LMMB QA program prescribed minimum standards to which all organizations collecting data were required to adhere. The quality activities implemented for the mercury monitoring portion of the study are further described in Section 2.6 and included use of standard operating procedures (SOPs), training of laboratory and field personnel, and establishment of method quality objectives (MQOs) for study data. A detailed description of the LMMB quality assurance program is provided in *The Lake Michigan Mass Balance Study Quality Assurance Report* (USEPA, 2001b). A brief summary of the quality of atmospheric mercury data is provided below.

Quality Assurance Project Plans (QAPPs) were developed by the PIs and were reviewed and approved by GLNPO. Each researcher trained field personnel in sample collection SOPs prior to the start of the field season and analytical personnel in analytical SOPs prior to sample analysis. Each researcher submitted test electronic data files containing field and analytical data according to the LMMB data reporting standard prior to study data submittal. GLNPO reviewed these test data sets for compliance with the data reporting standard and provided technical assistance to the researchers. In addition, each researcher's laboratory was audited during an on-site visit at least once during the time LMMB samples were being analyzed. The auditors reported positive assessments and did not identify issues that adversely affected the quality of the data.

As discussed in Section 2.6, data verification was performed by comparing all field and quality control (QC) sample results produced by each PI with their MQOs and with overall LMMB Study objectives. Analytical results were flagged when pertinent QC sample results did not meet acceptance criteria as defined by the MQOs. These flags were not intended to suggest that data were not useable; rather they were intended to caution the user about an aspect of the data that did not meet the predefined criteria. Table 3-5 provides a summary of flags applied to the atmospheric mercury data. The summary includes the flags that directly relate to evaluation of the MQOs to illustrate some aspects of data quality, but does not include all flags applied to the data to document sampling and analytical information, as discussed in Section 2.6. One result for vapor mercury was qualified as invalid, and was not used in the analyses of atmospheric mercury concentrations presented in this report.

Table 3-5. Summary of Routine Field Sample Flags Applied to Mercury in Atmospheric Samples

| Flag | Number of QC Samples | | | Percentage of Samples Flagged (%) | | |
|---|---|---|---|---|---|---|
| | Particulate | Precipitation | Vapor | Particulate | Precipitation | Vapor |
| LOB, Low Biased Result | — | — | — | 1% (5) | 0 | 0 |
| INV, Invalid Result | — | — | — | 0 | 0 | 0.3% (1) |
| FFD, Failed Field Duplicate | — | 33 | — | — | 1% (2) | — |
| FFT, Failed Trip Blank | 43 | — | 45 | 1% (2) | 0 | 0.3% (1) |
| FPC, Failed Lab Performance Check | 219 | 846 | 375 | 1% (5) | 0 | 0 |
| MDL, Below Method Detection Limit | NA | — | NA | NA | 0 | NA |
| SDL, Below System Detection Limit | — | NA | — | 0 | NA | 0 |

The number of routine field samples flagged is provided in parentheses. The summary provides only a subset of applied flags and does not represent the full suite of flags applied to the data.
NA = Not Applicable

The analytical sensitivity of precipitation routine field samples was assessed through comparison to a method detection limit (MDL) of 0.300 ng/L. For particulate and vapor field samples, analytical sensitivity was assessed through comparison to system detection limits (SDL) equaling 1.00 pg/m$^3$ and 0.200 ng/m$^3$, respectively. If a sample result was below its appropriate limit, a “below MDL” or “below SDL” flag was to be applied to that sample. However, because all sample concentrations were above the corresponding limit, the MDL and SDL flags were not applied to any sample.

Field trip blanks were analyzed to assess the potential for contamination of routine field samples. A total of 88 trip blanks were analyzed, 45 in the vapor phase, and 43 in the particulate phase. In accordance with the researcher’s data qualifying rules, samples were flagged for trip blank contamination (FTB) if the associated blank concentration exceeded the SDL expressed as a mass (43.45 pg for particulate samples and 0.084 ng for vapor samples). In the particulate phase, two samples were flagged for trip blank contamination, based on associated blank masses 68.2 pg and 79.1 pg. The flagged particulate routine field sample results, when expressed as masses, were approximately two and ten times the associated blank masses. One additional sample in the vapor phase was flagged for blank contamination due to an associated blank mass of 0.205 ng. The flagged vapor sample had a mass approximately 5 times greater than the associated blank mass.

A total of 33 field duplicate samples were collected and analyzed to assess precision for the precipitation phase. Field duplicates were collected at three of the five stations from which precipitation samples were collected. In accordance with the researcher’s data qualifying rules for field and laboratory duplicates, samples were flagged for a failed duplicate (FFD) if the relative percent difference (RPD) between results for a sample and its duplicate was greater than 25%. Two field duplicate pairs failed to meet this criteria, with RPDs of 25.7% and 62.5%. No field duplicate samples were collected for the particulate or vapor phases; therefore, the FFD flag was not applied to any samples from these phases.

Laboratory performance check samples were used to monitor analytical bias. Performance check samples were run after every 6 samples, resulting in 1,440 total check samples. In accordance with the researcher's data qualifying rules for performance checks, field samples were flagged for a failed performance check (FPC) if the absolute percent difference for the associated performance check was greater than 20%. The FPC flag was applied to five particulate field samples, due to performance check percent differences of -28.8% and -29.1% (corresponding to percent recoveries of 71.2% and 70.9%, respectively). These five samples were also qualified as being low biased by the QC Coordinator due to the performance check recoveries. No other samples were qualified as being low biased or high biased based on analyses of performance checks, blank contamination, or other internal QC data.

As discussed in Section 1.5.5, MQOs were defined in terms of six attributes: sensitivity, precision, accuracy, representativeness, completeness, and comparability. GLNPO derived data quality assessments based on a subset of these attributes. For example, system precision was estimated as the mean RPD between the results for field duplicate pairs. Similarly, analytical precision was estimated as the mean RPD between the results for laboratory duplicate pairs. Table 3-6 provides a summary of data quality assessments for several of these attributes for atmospheric data.

Table 3-6. Data Quality Assessment for Mercury in Atmospheric Samples

| Parameter | Assessment | | |
|---|---|---|---|
| | Particulate | Precipitation | Vapor |
| Number of Routine Samples Analyzed | 399 | 407 | 393 |
| System Precision, Mean Field Duplicate RPD (%), >SDL | — | 9.78% (33) | — |
| Analytical Bias, Mean LPC RPD% | - 2.20% (219) | 0.823% (846) | - 1.51% (375) |
| Analytical Sensitivity, Samples reported as <SDL or MDL (%) | 0 | 0 | 0 |

Number of QC samples used in the assessment is provided in parentheses
SDL = System detection limit
LPC = Laboratory performance check

The mean RPD between routine field samples and field duplicates for mercury in precipitation was 9.78%, indicating good precision. Because field duplicates were collected and reported for the precipitation phase only, no estimate of system precipitation could be made for the particulate and vapor phases. For these two phases, the PI collected and analyzed collocated samples. Because collocated samples were collected at only one of the sites and because the sampling times for these samples were shorter than for the routine field samples, these results may not fully represent the variability that may have been observed for field samples. Therefore, results for the collocated samples were not used in the QA assessment.

Analytical results for laboratory duplicates were not reported as individual results. The PI reported average results; however, the number of replicates that were included in the average or the standard deviation of those results were not provided. Based on submitted results, the results for laboratory duplicates could not be verified. Therefore, no estimate of analytical precision could be made for the atmospheric data.

Analytical bias was evaluated by calculating the mean RPD of laboratory performance check samples (LPC). Results indicated very little overall bias for analytical results. Mean LPC RPDs for the three phases ranged from -2.20% for particulate to 0.823% for precipitation. When expressed as percent recoveries, these means correspond to 97.8% and 101%, respectively.

Analytical sensitivity was evaluated by calculating the percentage of samples reported below the SDL for precipitation data and the percentage of samples reported below the MDL for the particulate and vapor data. This percentage was 0% for all three phases.

## 3.3 Data Interpretation

### 3.3.1 Atmospheric Sources

Based on the results of this study, vapor, particulate and precipitation phases were all important sources of mercury to Lake Michigan. All results from all three phases were above the associated method or system detection limit. The mean vapor and particulate mercury concentrations of 2.44 ng/m$^3$ and 30.7 pg/m$^3$ (0.0307 ng/m$^3$) were approximately 12 and 30 times greater than their associated SDLs. The mean precipitation-phase mercury concentration of 20.6 ng/L was approximately 70 times greater than the associated MDL.

### 3.3.2 Seasonal Considerations

Generally, the effect of season on mercury concentration depended on the phase and the station from which the samples were collected. For vapor-phase mercury, significant differences between seasons were observed only at IIT Chicago and Chiwaukee Prairie, with peak concentrations during the summer at both stations. Both of these stations had greater levels in the summer of 1994 compared to 1995. For particulate-phase mercury, significant seasonal differences were observed only at Sleeping Bear Dunes, with peak concentrations occurring during the summer.

Seasonal patterns were most apparent in precipitation-phase mercury. Significant differences between seasons occurred at four of the five stations. For each of these stations, the peak concentrations occurred in summer and the lowest concentrations occurred either during autumn or winter. However, these seasonal differences may have been partly due to the occurrence of smaller precipitation events during the summer, compared to other seasons, which would result in smaller sample volumes, and hence, higher mercury concentrations, during the initial wash out of mercury from the atmosphere.

When the data were examined using volume-weighted means, seasonal patterns became much less distinct. However, for all stations other than Chicago IIT, the lowest volume-weighted means did occur during the winter. This may have been due to differences in precipitation type, as the relationship between mercury and precipitation may differ between warm-cloud processes and cold-cloud processes (Landis *et al.*, 2002). In a study of precipitation in mercury in the Lake Superior region, Glass *et al.* (1986) found significantly greater mercury concentrations in rainfall than in snow. The seasonal pattern was also similar to that observed at three sites in Wisconsin as part of the National Atmospheric Deposition Program's (NADP) Mercury Deposition Network (WDNR, 1999). Volume-weighted mean concentrations in that study were highest in the spring or summer for each site for all three years, other than for one site in 1995, where the mean concentration was highest in the winter.

Significant differences between seasons were observed at only one LMMB station for particulate-phase mercury. At the Sleeping Bear Dunes site, the mean concentration during summer was significantly greater than the mean concentration during winter. This result is not consistent with results from past studies. Particulate-phase mercury concentrations have previously been observed to be greater during the winter compared to the summer in Maryland (Mason *et al.*, 1997) and near Lake Michigan (Keeler *et al.*, 1995). Concentrations at Sleeping Bear Dunes were similar during the two summers for which data were collected.

### 3.3.3 Regional Considerations

For particulate and vapor-phase mercury, the mean concentration at IIT Chicago was significantly greater than those at the other stations. For precipitation-phase mercury, the mean concentration was also greatest at IIT Chicago, and was significantly higher than at two of the other stations. This was not unexpected, as IIT Chicago was the only one of the five stations that could be classified as being located in an urban area. It has been observed in the past that the Chicago area has significantly increased mercury levels in dry deposition (Keeler, 1994) and precipitation around local urban/industrial areas (Hoyer *et al.*, 1995). The difference between IIT Chicago and the other stations was greater for particulate-phase mercury than for the other phases. This may be due to the greater prevalence of the mercuric form of mercury ($Hg^{2+}$) in the particulate phase compared to the vapor phase. Mercuric mercury is more soluble in water, and therefore more likely to be due to local sources (Lindberg and Stratton, 1998). Mason *et al.* (1997) found low levels of ionic mercury in precipitation, and hypothesized that this was due to in-cloud oxidation processes being a significant source of mercury in precipitation, rather than just the scavenging of particles or of gaseous ionic mercury.

The mean and median vapor-phase concentrations at IIT Chicago (mean: 3.62 ng/m$^3$, median: 2.90 ng/m$^3$) were very close to those collected in Egbert, Ontario in 1990 (mean: 3.71 ng/m$^3$, median: 2.90 ng/m$^3$) by Schroeder and Markes (1994). The station at IIT Chicago represents a major urban/industrial area and the station in the Ontario study was located near Toronto, another major urban/industrial area. Thus, the results from both studies may represent the influences of urban and industrial sources of mercury. However, the samples from the Ontario study were all collected in the months of March and April, and therefore cannot be interpreted as an annual estimate. The 49 mercury samples collected at IIT Chicago in March and April 1995 had a mean of 2.26 ng/m$^3$ and a median of 2.14 ng/m$^3$, substantially lower than the overall values. In addition to collecting samples in Egbert, Ontario, Schroeder and Markes (1994) also measured mercury at Pt. Petre, Ontario. This site had lower mercury concentrations, with a mean of 2.21 ng/m$^3$, comparable to the other stations in the LMMB data set. The Pt. Petre samples were collected in the autumn only, however, and the LMMB stations had slightly lower results during these months.

While the difference in mean precipitation-phase mercury concentrations at IIT Chicago and the other stations was not as large compared to the other phases in the study, the mean concentration at IIT Chicago was still higher than for many sites in other studies. For example, samples of mercury in precipitation have recently been collected as part of the National Atmospheric Deposition Program's Mercury Deposition Network (MDN). The volume-weighted mean calculated from the MDN transition phase in 1995 was 10.25 ng/L, lower than the mean at all five LMMB stations (MDN, 1999). In addition, in an assessment using data collected as part of the NADP, volume-weighted mean concentrations were calculated for samples collected from seven sites in Wisconsin from 1995 to 1997 (WDNR, 1999). The state-wide volume-weighted means for the three years ranged from 11.48 ng/L in 1997 to 15.75 ng/L in 1995. These means are similar to the volume-weighted mean concentrations from Chiwaukee Prairie (16.5 ng/L), Bondville (16.1 ng/L), and South Haven (13.9 ng/L), but below the volume-weighted mean of 21.1 ng/L from IIT Chicago. However, the maximum annual volume-weighted mean of 25.60 ng/L from the seven Wisconsin sites, occurring at the rural Wildcat Mountain State site in western Wisconsin in 1996, exceeded the volume-weighted mean at IIT Chicago. This mean was based on the results from one of two sampling columns at that site, with the other column yielding in a mean of 13.81 ng/L. It is worth noting that the mean concentration from this second column was greater than that of Sleeping Bear Dunes (11.0 ng/L), the only atmospheric site from the LMMB located in a similarly rural area.

Other recent studies have also shown spatial differences in mercury concentration in precipitation. Mason *et al.* (2000) found higher levels of mercury flux at a site in Baltimore, compared to three other rural sites in Maryland. Glass *et al.* (1986) measured mercury concentrations in snow pack collected from three areas in Minnesota, one in Wisconsin, one in Upper Peninsula of Michigan, and one in Ontario within watersheds that drain into Lake Superior. Samples of snow pack were collected at 10 to 17 specific locations in each of these geographic areas. Measurements of mercury in snow from five of the six areas were below those of IIT Chicago in this study. The means from these five areas ranged from 12 ng/L to 15 ng/L, with standard deviations ranging from 1 to 5 ng/L. The sixth sampling area was centered around Grand Rapids, Minnesota, and had a mean concentration of 100 ng/L and a standard deviation of 173 ng/L. The mean concentration is substantially higher than the mean at IIT Chicago in this study, and may be the result of contamination of samples from that area, or may represent a localized source of mercury. In addition, the results may not be comparable to all of the LMMB data, because the samples were collected in snow, rather than rain.